

Supporting Information

A kinetic study on the efficient formation of high-valent Mn(TPPS)-oxo complexes by various oxidants

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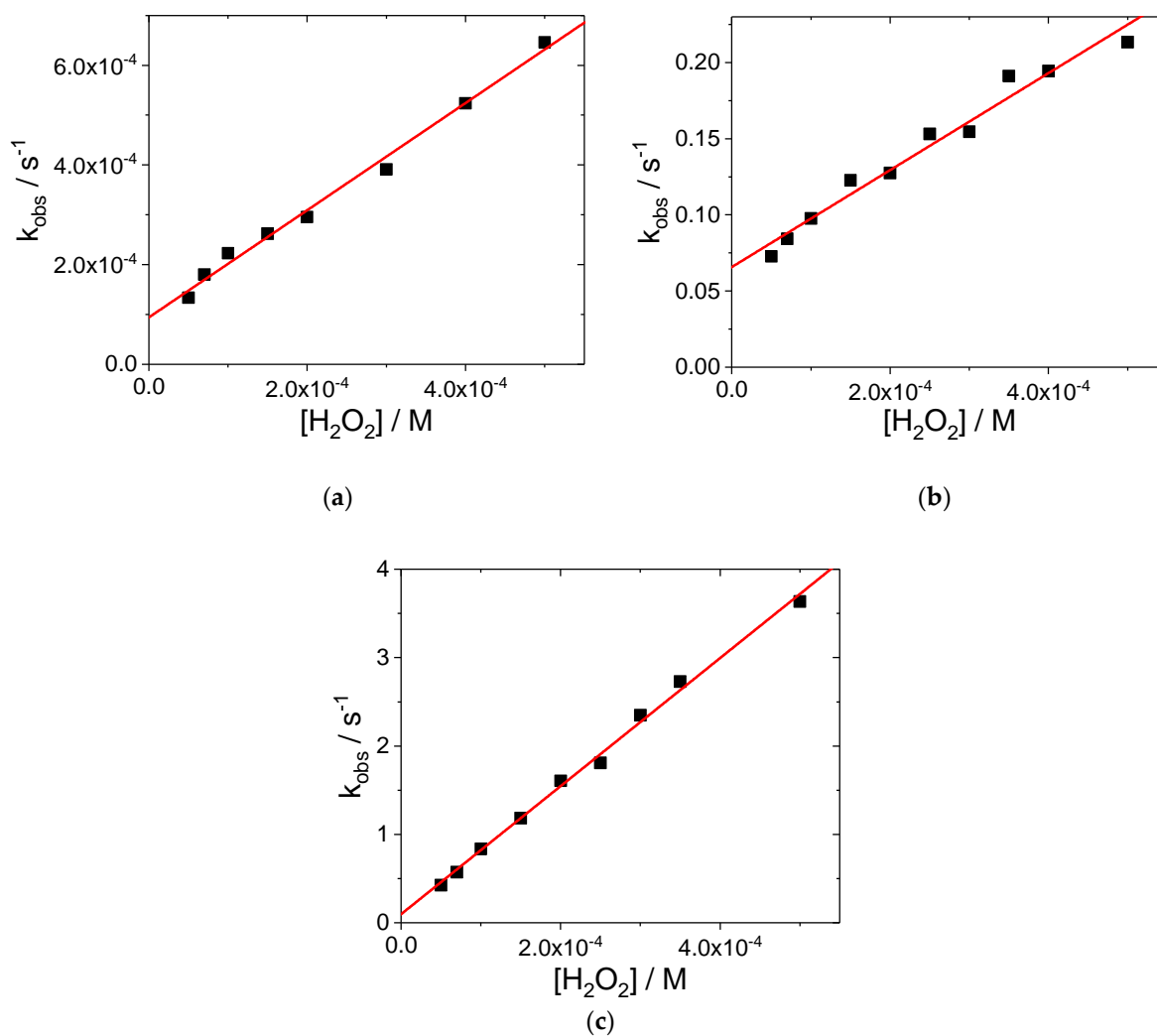


Figure S1. Plots of k_{obs} versus H_2O_2 concentration for the reaction of $\text{Mn}^{\text{III}}(\text{TPPS})$ with H_2O_2 at pH = 9.3: (a) in NaOH solution; (b) in 0.5 M KNO_3 solution with addition of NaOH; (c) in 0.5 M carbonate buffer. Experimental conditions: $[\text{Mn}^{\text{III}}(\text{TPPS})] = 6 \mu\text{M}$, $[\text{H}_2\text{O}_2] = 50 - 500 \mu\text{M}$, $T = 25 \text{ }^\circ\text{C}$.

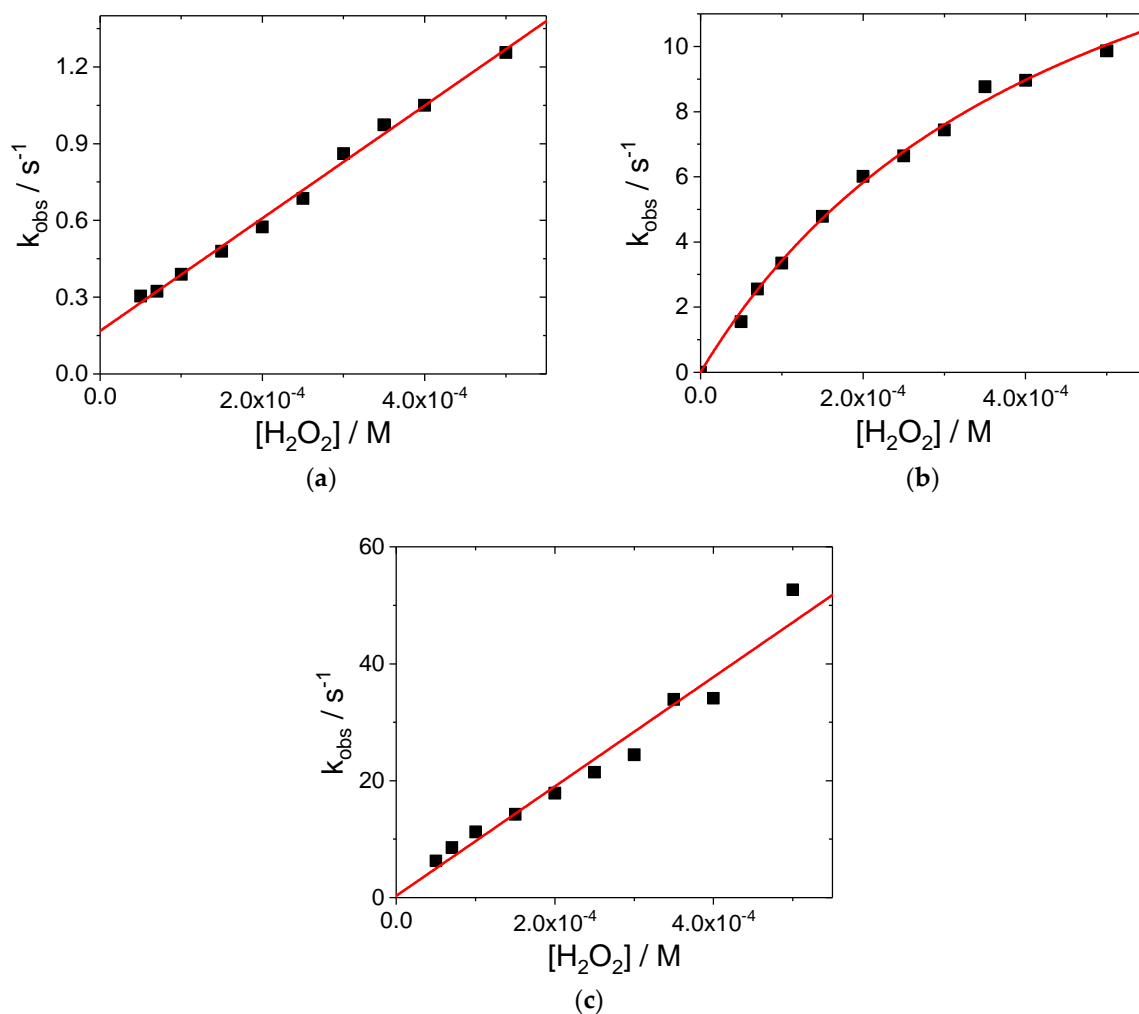


Figure S2. Plots of k_{obs} versus H_2O_2 concentration for the reaction of $\text{Mn}^{\text{III}}(\text{TPPS})$ with H_2O_2 at pH = 11: (a) in NaOH solution; (b) in 0.5 M KNO_3 solution with addition of NaOH; (c) in 0.5 M $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$ solution. Experimental conditions: $[\text{Mn}^{\text{III}}(\text{TPPS})] = 6 \mu\text{M}$, $[\text{H}_2\text{O}_2] = 50 - 500 \mu\text{M}$, $T = 25 \text{ }^\circ\text{C}$.

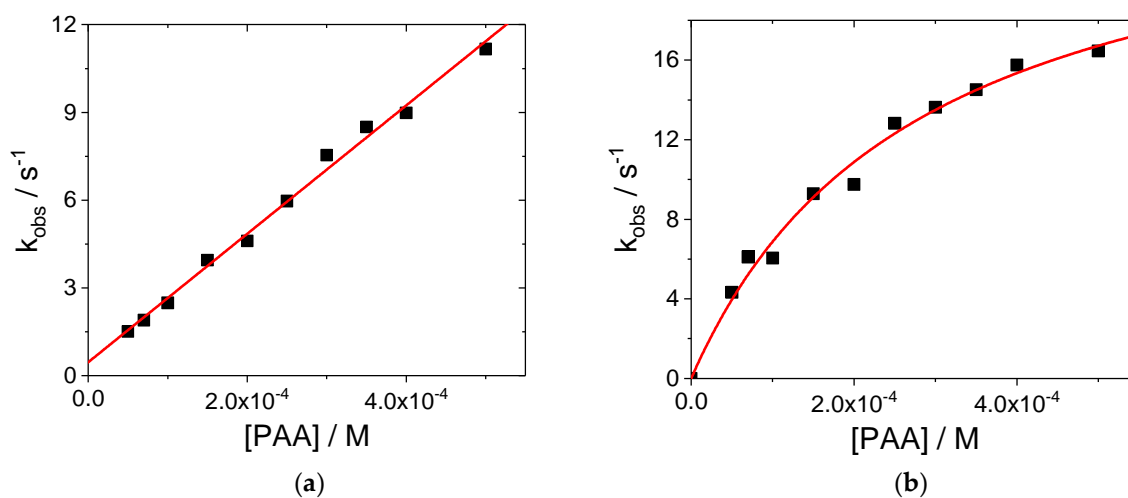


Figure S3. Dependence of k_{obs} on [PAA] for the reaction of $\text{Mn}^{\text{III}}(\text{TPPS})$ with PAA at pH = 11: (a) in NaOH solution; (b) in 0.5 M KNO_3 solution with addition of NaOH. Experimental conditions: $[\text{Mn}^{\text{III}}(\text{TPPS})] = 6 \mu\text{M}$, $[\text{PAA}] = 50 - 500 \mu\text{M}$, $T = 25 \text{ }^\circ\text{C}$.

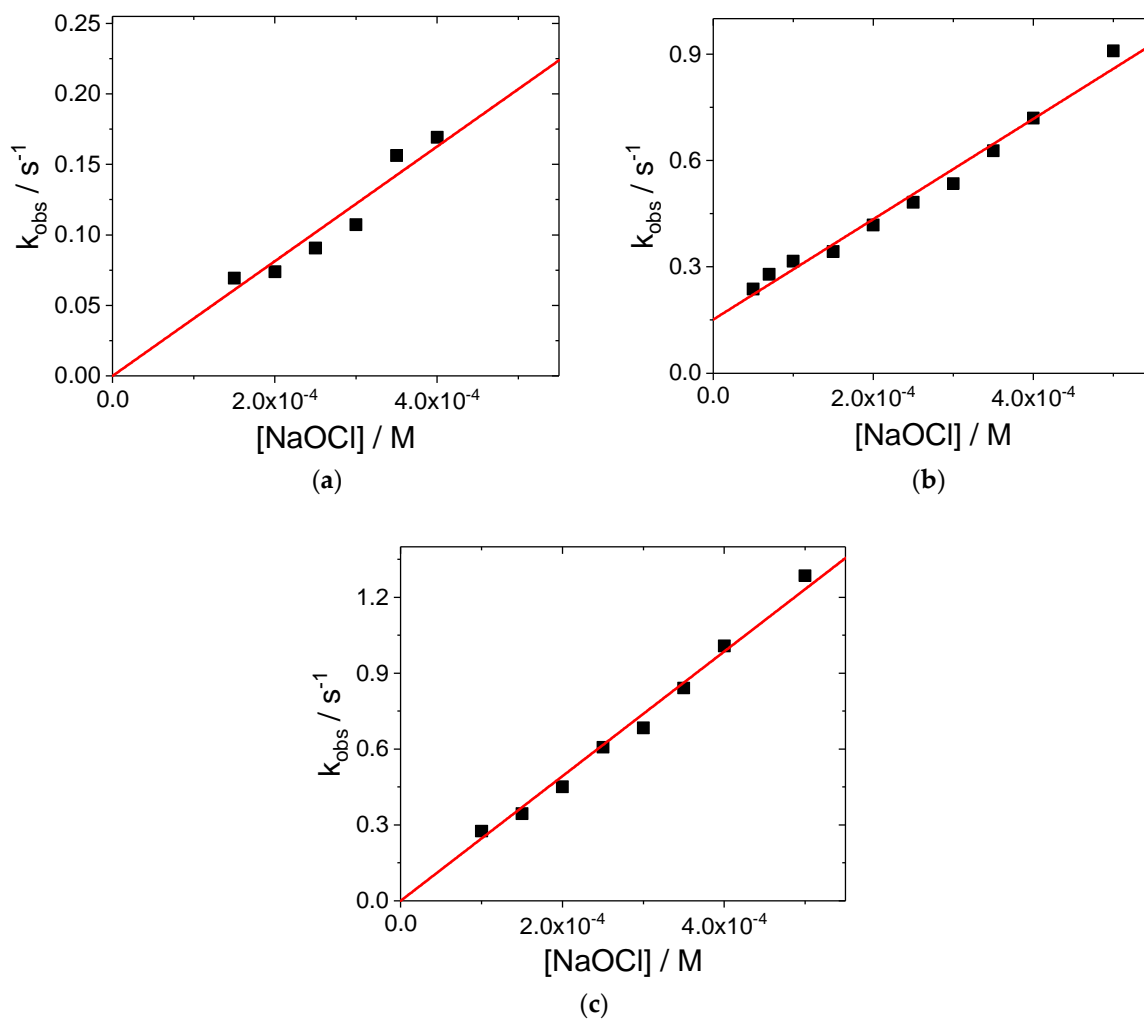


Figure S4. Plots of k_{obs} versus NaOCl concentration for the reaction of $\text{Mn}^{\text{III}}(\text{TPPS})$ with H_2O_2 at pH = 9.3: (a) in NaOH solution; (b) in 0.5 M KNO_3 solution with addition of NaOH; (c) in 0.5 M $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$ solution. Experimental conditions: $[\text{Mn}^{\text{III}}(\text{TPPS})] = 6 \mu\text{M}$, $[\text{NaOCl}] = 50 - 500 \mu\text{M}$, $T = 25 \text{ }^\circ\text{C}$.

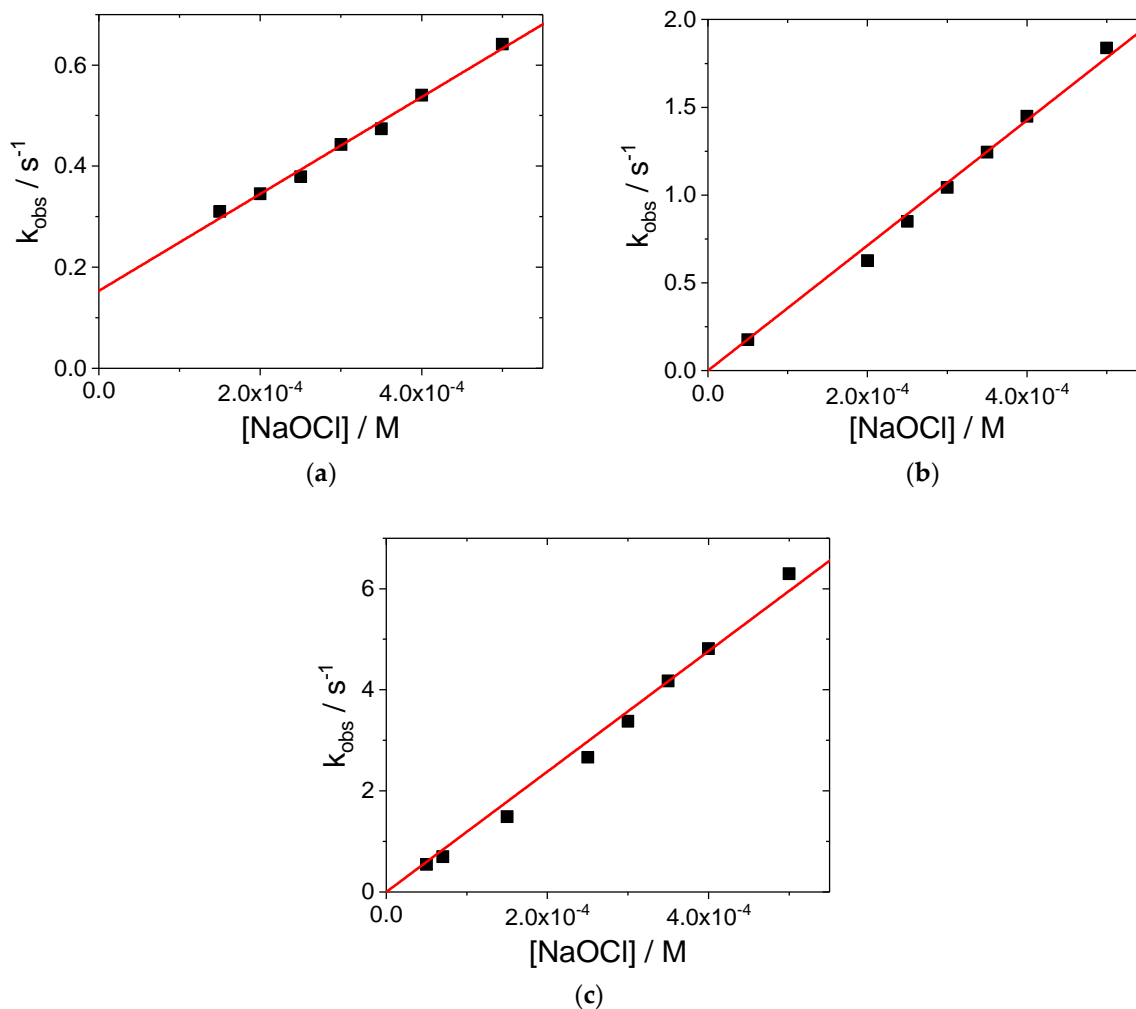


Figure S5. Dependence of k_{obs} on $[\text{NaOCl}]$ for the reaction of $\text{Mn}^{\text{III}}(\text{TPPS})$ with NaOCl at $\text{pH} = 11$: (a) in NaOH solution; (b) in 0.5 M KNO_3 solution with addition of NaOH ; (c) in $0.5 \text{ M Na}_2\text{CO}_3 + \text{NaHCO}_3$ solution. Experimental conditions: $[\text{Mn}^{\text{III}}(\text{TPPS})] = 6 \mu\text{M}$, $[\text{PAA}] = 50 - 500 \mu\text{M}$, $T = 25 \text{ }^\circ\text{C}$.

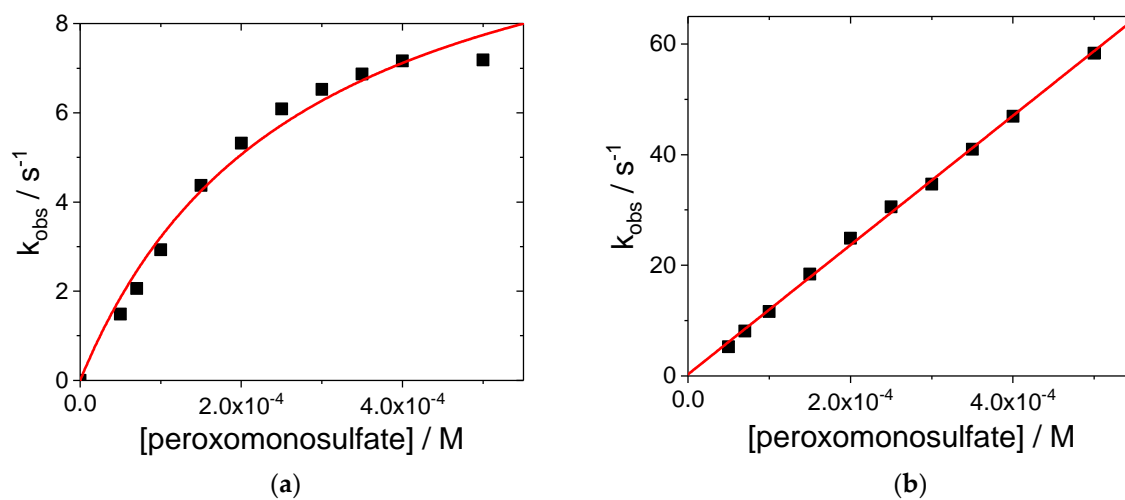


Figure S6. Plots of k_{obs} versus persulfate concentration for the reaction of $\text{Mn}^{\text{III}}(\text{TPPS})$ with peroxomonosulfate at $\text{pH} = 11$: (a) in 0.5 M KNO_3 solution with addition of NaOH ; (b) in $0.5 \text{ M Na}_2\text{CO}_3 + \text{NaHCO}_3$ solution. Experimental conditions: $[\text{Mn}^{\text{III}}(\text{TPPS})] = 6 \mu\text{M}$, $[\text{peroxomonosulfate}] = 50 - 500 \mu\text{M}$, $T = 25 \text{ }^\circ\text{C}$.

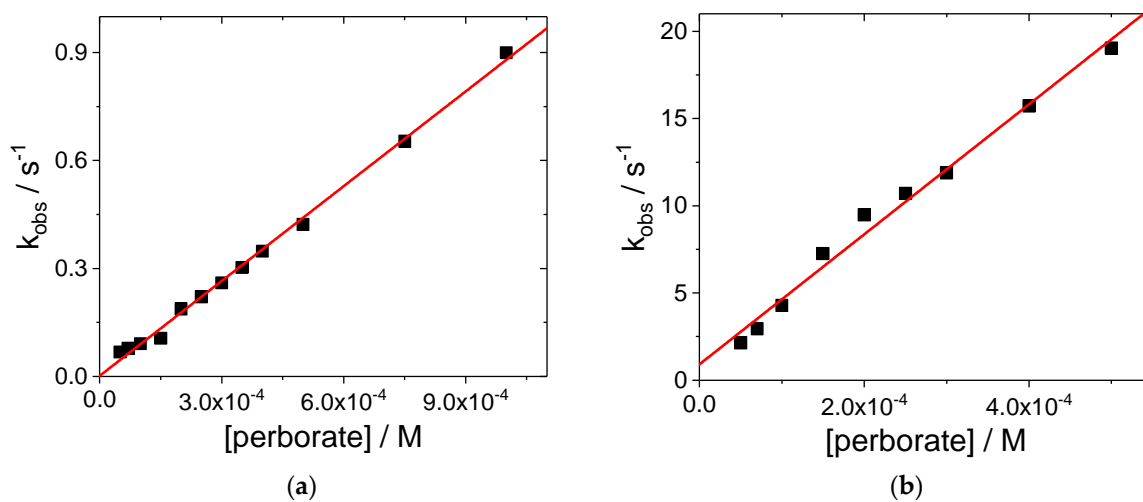


Figure S7. Dependence of k_{obs} on [perborate] for the reaction of $\text{Mn}^{\text{III}}(\text{TPPS})$ with perborate at pH = 11: (a) in 0.5 M KNO_3 solution with addition of NaOH; (b) in 0.5 M $\text{Na}_2\text{CO}_3 + \text{NaHCO}_3$ solution. Experimental conditions: $[\text{Mn}^{\text{III}}(\text{TPPS})] = 6 \mu\text{M}$, $[\text{perborate}] = 50 - 500 \mu\text{M}$, $T = 25 \text{ }^\circ\text{C}$.